

## Electrophysical properties of polychlotriftoethylene-carbonile iron system at low and high frequencies

*S.M.Makhno*<sup>1,2,3</sup>, *O.M.Lisova*<sup>3</sup>, *P.P.Gorbyk*<sup>3</sup>,  
*G.M.Gunya*<sup>3</sup>, *M.T.Kartel*<sup>1,2,3</sup>

<sup>1</sup>Ningbo University of Technology, 201 Fenghua Road,  
315211 Ningbo, China

<sup>2</sup>Ningbo Sino-Ukrainian New Materials Industrial Technologies Institute,  
Kechuang building, N777 Zhongguan road, 315211 Ningbo, China

<sup>3</sup>O.Chuiko Institute of Surface Chemistry, National Academy of Sciences  
of Ukraine, 17 General Naumov Str., 03164 Kyiv, Ukraine

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The samples of polychlotrifluoroethylene (PCTFE) — carbonyl iron (CI) with a 0–0.2 volume fraction of the filler was obtained by the method of thermal pressing of the polymer melt. The electrophysical and magnetic properties of the PCTFE-CI system samples in the ultra-high frequency range and at low frequencies were investigated by impedance spectrometry, two-contact method, and by using a high-frequency interferometer. It is shown that the real  $\epsilon'$  and the imaginary  $\epsilon''$  components of the complex dielectric constant  $\epsilon^*$  are reduced by 10 % in the range of 8–12 GHz due to the frequency dispersion of the filler properties. When the content of CI in the polymer is above the percolation threshold, the dependence of electrical conductivity on frequency is absent in the range of  $10^{-2}$  –  $10^5$  Hz. Using the contactless induction method, the maximum surface charge of PCTFE-CI film composites was observed at a content of CI somewhat below the percolation threshold in the system. It is shown that the composites have stable characteristics up to a temperature of 90°C. The magnetic properties of the ferromagnetic materials have a maximum in the microwave range due to the high-frequency losses associated with the precession of magnetization in its own internal field (anisotropy field) of the magnetic material. Natural ferromagnetic resonance (NFR) occurs when the frequency of the external electromagnetic field coincides with the frequency of precession of the magnetic moment in the intra-domain field. The change in the values of  $\mu'$  and  $\mu''$  in the range of 4 – 10.5 GHz is probably related to the resonant nature of the interaction of the short circuit with electromagnetic radiation, and the mechanism of absorption of microwave radiation with the natural ferromagnetic resonance of the short circuit at such frequencies.

**Keywords:** microwave band, ferromagnetic resonance, percolation threshold, carbonyl iron.

**Електрофізичні властивості системи поліхлотрифторетилен-карбонільне залізо на низьких та високих частотах.** *С.М.Махно, О.М.Лісова, П.П.Горбик, Г.М.Гуня, М.Т.Картель*

Методом термічного пресування з розплаву полімеру одержано зразки системи поліхлотрифторетилен (ПХТФЕ)-карбонільне залізо (КЗ) в межах 0–0,2 об'ємної долі наповнювача. Електрофізичні і магнітні властивості зразків системи ПХТФЕ-КЗ в надвисокочастотному діапазоні та на низьких частотах досліджено методами імпедансної спектрометрії, двоcontactним методом та за допомогою надвисокочастотного інтерферометра. Показано, що  $\epsilon'$  і  $\epsilon''$  в діапазоні 8 – 12 ГГц знижується на 10 % за рахунок частотної дисперсії властивостей наповнювача. Для вмісту КЗ у полімері після порогу перколяції залежність електропровідності від частоти відсутня в діапазоні  $10^{-2}$  –

$10^5$  Гц. За допомогою безконтактного індукційного методу проведено дослідження поверхневого заряду плівкових композитів системи ПХТФЕ-КЗ, встановлено, що максимум поверхневого заряду спостерігається при вмісті КЗ дещо нижчому, ніж значення порогу перколяції в системі. Показано, що композити системи мають стабільні характеристики до температури  $90^\circ\text{C}$ . Зміна значень  $\mu'$  та  $\mu''$  в діапазоні 4–10,5 ГГц, вірогідно, пов'язана з резонансним характером взаємодії КЗ з електромагнітним випромінюванням, а механізм поглинання НВЧ випромінювання з природним феромагнітним резонансом КЗ на таких частотах.

## 1. Introduction

The modern technologies allow us to obtain particles of metals and their compounds of predetermined compositions and sizes [1], as well as to form spatial structures with important functional properties with the help of various matrices and stabilizing systems [2]. The miniaturization of devices and appliances requires the optimal use of each component material. Composite systems with ferromagnetic and antiferromagnetic inclusions distributed in a dielectric matrix have unique physical properties. The use of such systems, which have specific properties of components, allows the formation of functional composite materials for the creation of magnetic sensors, positioning systems, magnetic strips and magnetic dampers [3].

Obtaining metal-dielectric matrix composites is possible in many ways. The known methods of synthesis of metal-filled composites include the treatment of polymer films with metal vapors; chemical reactions of metal salts in polymer solutions, followed by removal of the polymer; polymerization of metal-containing monomer systems; obtaining the composite in the polymerization process of the matrix from the state of a viscous homogeneous mixture.

The most reproducible and technological methods of obtaining polymer composites is the method of molding the polymer melt under specified conditions: temperature and pressure. For composites with a magnetic filler, the defining characteristic is the frequency dependence of the complex magnetic and dielectric permittivity in a wide range of wavelengths. The composition and structure of such a composite material determines its useful characteristics, where electrical contacts between the particles play a decisive role.

Fillers that actively exhibit their properties in the polymer composite are magnetodielectrics (ferromagnets, the particles of which are separated by insulating films of non-magnetic material). The magnetic properties of magnetodielectrics are determined by the size and shape of the ferromagnetic

particles, their relative location, the quantitative ratio between the ferromagnet and the dielectric. Carbonyl iron (CI), which is 98 % composed of pure iron with impurities of carbon and nitrogen, has stable properties and belongs to high-frequency magnetic materials.

The aim of this study is to study the variation of the dielectric and magnetic properties of the PCTFE-CI system in the microwave range and at low frequencies.

## 2. Experimental

For the manufacture of composites, a crystalline-amorphous polymer of polychlorotrifluoroethylene (PCTFE) F-3M grade A and CI GOST 9849-86 was used. The samples for PCTFE-CI systems were obtained by pressing at 495 K and 2 MPa.

The real  $\varepsilon'$  and the imaginary  $\varepsilon''$  components of the complex dielectric constant  $\varepsilon^*$  were measured at frequencies of 8 – 12 GHz using an ultra-high frequency interferometer [4]; and the temperature dependences of electrical conductivity at low frequencies were investigated by a two-contact method using an E7-14 impedance meter in the range of 443 K.

The frequency dependences of the real and imaginary component of the complex dielectric constant and the electrical conductivity  $\sigma^*$  of the PCTFE-CI composites were determined by calculating the  $Z^*$  impedance spectra in the frequency range of  $10^{-1} - 10^6$  Hz obtained on a Solartron SI 1260 impedance spectrometer.

Impedance measurements of PCTFE-CI composites were performed at room temperature, in the concentration range from 0 to 0.2 volume fraction ( $\varphi$ ) of CI. Complex dielectric permittivity and electrical conductivity were calculated according to the classical equations of electrical engineering using an equivalent electrical circuit with capacitance and resistance connected in parallel. The value of the complex resistivity  $\rho^*$  at a certain frequency was defined as

$$\rho^* = \rho' + i\rho'' = Z^* \cdot \frac{S}{h}, \quad (1)$$

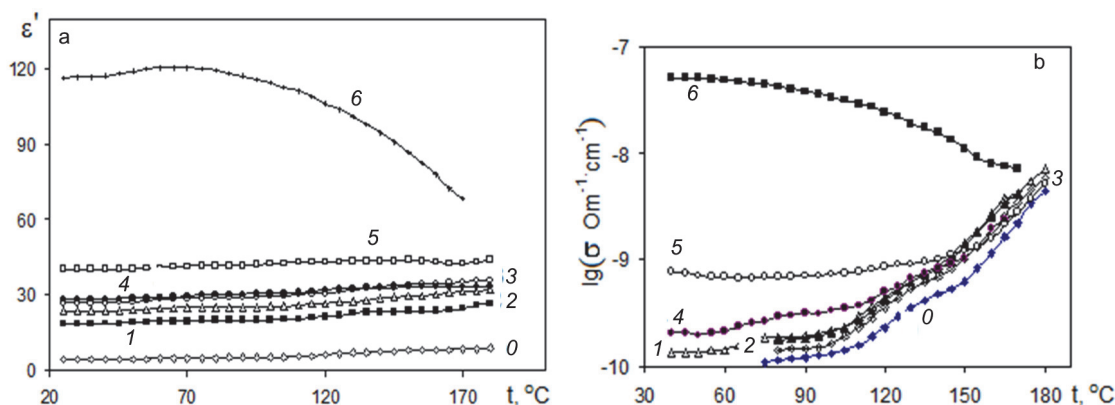


Fig. 1. The real component of the complex dielectric constant (a) and conductivity (b) as a function of temperature at a frequency of 1 kHz for the PCTFE-CI system with the CI volume content: 0 — 0; 1 — 0.04; 2 — 0.06; 3 — 0.09; 4 — 0.13; 5 — 0.16; 6 — 0.2.

where  $S$  and  $h$  are the area and thickness of the specimen. Complex specific electrical conductivity was determined according to

$$\sigma^* = \sigma' + i\sigma'' = \frac{1}{\rho^*}. \quad (2)$$

The values of the complex dielectric constant were calculated from the values of the complex impedance according to the expressions:

$$\epsilon' = \frac{-Z''}{\omega \cdot \epsilon_0 \cdot (Z'^2 + Z''^2)} \cdot \frac{S}{h}, \quad (3)$$

$$\epsilon'' = \frac{Z'}{\omega \cdot \epsilon_0 \cdot (Z'^2 + Z''^2)} \cdot \frac{S}{h}, \quad (4)$$

where  $\omega = 2\pi f$  is the cyclic frequency of the electromagnetic field.

### 3. Results and discussion

The temperature dependences of the real component complex dielectric constant  $\epsilon'$  of the PCHTFE-CI system for the different volumetric contents of the CI have significant differences (Fig. 1a). For CI concentrations up to 0.08 volume fraction,  $\epsilon'$  does not significantly depend on temperature up to 180°C, which characterizes the stability of the composites. For the composite with  $\phi = 0.1$ , the temperature dependence  $\epsilon'$  has a maximum value of about 70°C, subsequently decreasing with increasing temperature.

The dependence of the electrical conductivity  $\sigma$  (Fig. 1b) on the temperature is more complicated. For composites with a CI volume content of up to 0.08, there is an increase in the  $\sigma$  values from 20 to 180°C by almost two orders of magnitude; and for

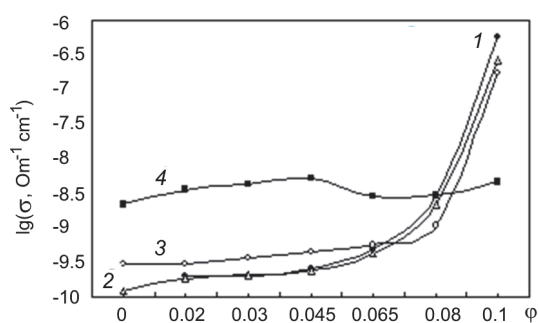


Fig. 2. Electrical conductivity of the PCTFE-CI system vs the CI volume content at different temperatures, °C: 1 — 40; 2 — 85; 3 — 125; 4 — 170 (at a frequency of 1 kHz).

a composite with  $\phi = 0.2$ , the electrical conductivity decreases by 6 times, which characterizes significant structural changes of composites due to surface phenomena.

The dielectric losses in the low frequency range are quite high and the values of  $\tan\delta$  reach 1 for the composite with  $\phi = 0.1$ . Fig. 2 shows that in the temperature range up to 125°C, the electrical conductivity increases sharply in the neighborhood of  $\phi = 0.06$ , which indicates the formation of percolation clusters. Up to 170°C, the change in temperature properties is observed poorly.

The surface charge density of the films of the PCTFE-CI system (Fig. 3) was determined by a noncontact induction method (oscillation of the electret in the capacitive gap) [5]. The change in the surface charge values is correlated with the nature of the conductivity change from the CI concentration to the short circuit, which is associated with the achievement of the percolation threshold. The lower the value of the perco-

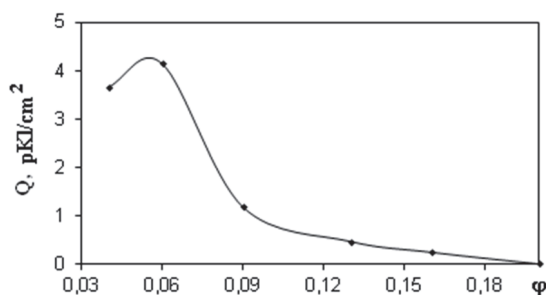


Fig. 3. The specific surface charge vs the content of the CI in the PCTFE-CI system.

lation threshold, the lower the concentration jumps values downward from the maximum (the charge of the system acquires maximum values at filler concentrations slightly lower than the percolation threshold of the system) to values that are several orders of magnitude smaller. The presence of surface charges in the composites beyond the percolation threshold can be explained by the presence of non-conducting areas on the surface of the polymer film where the charge accumulates. When the polymer is electrically conductive, the surface charge will go to zero. Therefore, the reduction of the specific charge after reaching the maximum value in the system with increasing concentration of short circuits is associated with the formation of a continuous percolation cluster.

On the frequency dependences of the real  $\sigma'$  component of the complex electrical conductivity (Fig. 4), the maxima and minima are not observed; Thus, at low frequencies, there is an area in which there is no frequency dependence of electrical conductivity, which corresponds to the through conductivity at direct current  $\sigma'_{ps}$ . As the frequency increases further, the conductivity increases according to the power law  $\sigma'_{nc}$ , where  $0 < n < 1$ . The similar nature of the dependence is described in the framework of the jump conduction model [6, 7] according to the equation:

$$\sigma'_{ps} = \sigma'_{nc} \cdot \left[ 1 + \left( \frac{\omega}{\omega_{av}} \right)^n \right], \quad (5)$$

where  $\omega_{av}$  is the average jump frequency of charge carriers. The exponent  $n$  is the same for all investigated concentrations in the polymer and is equal to  $\sim 0.8$ .

At low frequencies, the frequency dependence of electrical conductivity can be explained by the fact that the electrical con-

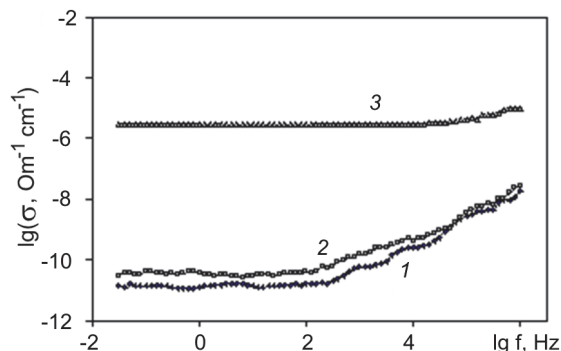


Fig. 4. Electrical conductivities as a frequency function for the PCTFE-CI system with the contents of the CI: 1 — 0.04; 2 — 0.09; 3 — 0.2.

ductivity at direct current significantly exceeds the contribution of the value  $(\omega/\omega_{av})$  equal to 0.8.

For composites with  $\phi \geq 0.1$ , the frequency dependence is not described by the equation (5), since the value of  $\sigma$  does not change until the frequency of  $10^5$  Hz; and at the frequency higher than  $10^5$  Hz, the contribution of the inductive component of the impedance becomes noticeable.

The frequency dependence of the dielectric loss tangent of the PCTFE system in the short-circuit mode is shown in Fig. 5a. The values of the dielectric constant decrease non-monotonically for both  $\epsilon'$  and  $\epsilon''$  in the specified frequency range, and the dielectric loss tangent has quite high values. The extrema of the frequency dependence are due to interference phenomena. The observed decrease in the values of  $\epsilon'$  and  $\epsilon''$  depending on the frequency can be explained by a decrease in the interaction between clusters when the wavelength of electromagnetic radiation decreases.

For the dependences of the components of the complex dielectric permittivity on the volume content of the short circuit (Fig. 5b), a change of the slope of the curves in the region  $\phi = 0.06$  is observed, which indicates the presence of a percolation transition in the PCTFE-CI system. The volume content of the short circuit, at which the percolation phenomenon occurs is the same for high and low frequencies due to the spherical shape of the filler microparticles and the uniform distribution of particles in the polymer matrix.

The real and imaginary parts of the complex magnetic permeability are different depending on the frequency of the alternating

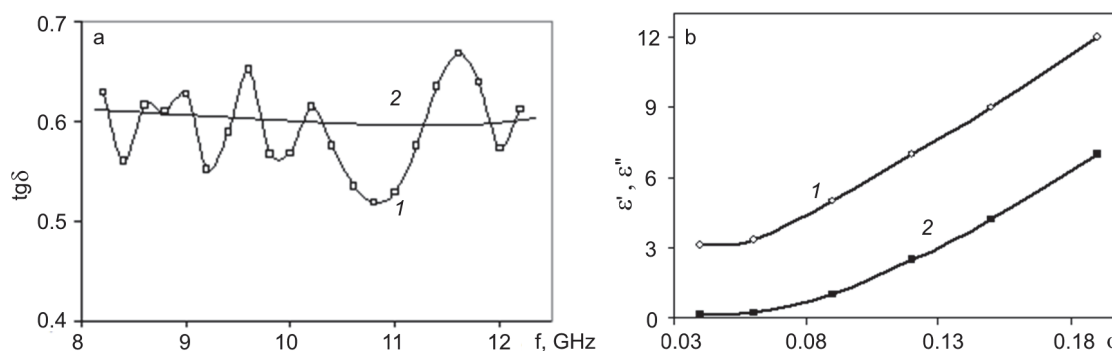


Fig. 5. (a) Dielectric loss tangent (1) and the trend line (2) as frequency functions for the PCTFE-CI system with 0.2 CI volume content; (b)  $\epsilon'$  (1) and  $\epsilon''$  (2) vs the CI volume content at the frequency of 10 GHz.

field and are characterized by magnetic spectra. The magnetic properties of ferromagnetic materials in the microwave range reach a maximum due to the high-frequency losses associated with the precession of magnetization in the intrinsic internal field (anisotropy field) of the magnetic material. Natural ferromagnetic resonance (NFR) occurs when the frequency of the external electromagnetic field coincides with the frequency of precession of the magnetic moment in the intra-domain field.

Generally, the effective field of anisotropy of a polycrystalline magnet is as follows

$$H_{ef} = H_A + H_\lambda + H_{mt}, \quad (6)$$

where  $H_A$  is the magnetic intensity of the crystallographic anisotropy;  $H_\lambda$  is the magnetic intensity of the magnetoelastic anisotropy caused by the residual mechanical stress in the material and possibly by external mechanical actions (the magnitude of the  $H_\lambda$  field in the ferrites is usually negligible);  $H_{mt}$  is the magnetizing magnetic tension of domain boundaries, depending on the mutual orientation of the boundaries and the vector of the alternating magnetic field.

The field of PFR frequencies in polycrystalline ferrites can be quite wide (from  $10^6$  to  $10^{10}$  Hz) and may partially overlap with the domain boundary resonance, which greatly complicates the form of the real spectrum. The spectrum of a real ferromagnetic resonance has  $\mu''$  maxima (at least two maxima).

The real and imaginary components of the complex magnetic permeability are experimentally determined at different frequencies in the microwave field; the results

are presented in Table 1. It can be seen

Table 1. The real  $\mu'$  and  $\mu''$  imaginary components of the complex magnetic permeability of CI in the microwave range

Frequency, GHz	$\mu'$	$\mu''$
4	1.53	0.54
6	2.35	1.95
8	2.45	1.55
10.3	1.45	1.25

from the table that in the region of 6–8 GHz, a maximum of resonant absorption of short-circuit particles is observed; probably, the indicated frequency range corresponds to the region of natural ferromagnetic resonance for CI.

#### 4. Conclusions

The electrophysical and magnetic properties of samples of the PCTFE-CI system were studied in the high-frequency and low-frequency ranges. It is shown that in the range of 8–12 GHz, the values  $\epsilon'$  and  $\epsilon''$  are reduced by 10 % due to the frequency dispersion of the properties of the filler. When the content of short-circuits in the polymer after the percolation threshold, the electrical conductivity is independent on the frequency in the range of  $10^{-2}$ – $10^5$  Hz.

It is shown that composites of the PCTFE-CI system have stable characteristics up to a temperature of 90°C.

The change in the values of  $\mu'$  and  $\mu''$  in the microwave range is probably associated with the resonant nature of the interaction, and the mechanism for the absorption of mi-

crowave radiation — with the natural ferromagnetic resonance of the microwave range.

It is shown that the maximum surface charge of the PCTFE-CI composites is observed when the CI content is slightly lower than the percolation threshold in the system.

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